

# PATENT ABSTRACTS OF JAPAN

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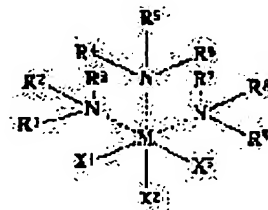
YOROZU KIYOTAKA

## (54) PRODUCTION OF ALPHA-OLEFIN OLIGOMER

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To obtain a useful  $\alpha$ -olefin oligomer such as 1-hexene at good efficiency by reacting an  $\alpha$ -olefin in the presence of a specified transition metal compound (e.g. (tripyridine) chromium chloride) and a specified aluminum compound.

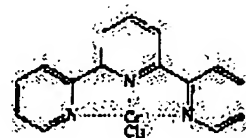
**SOLUTION:** This production process comprises the step of reaction an  $\alpha$ -olefin in the presence of a transition metal compound represented by formula I (wherein M is a transition metal; R1 to R9 are each H, OH, an alkyl or the like, provided that they may be suitably combined with each other; and X1 to X3 are each H, a halogen or an alkyl) and an aluminum compound represented by formula II (wherein R11 and R12 are each a 1-15C hydrocarbon group; X is a halogen;  $0 < m \leq 3$ ;  $0 \leq n < 3$ ;  $0 \leq p < 3$ ;  $0 \leq q < 3$ , and  $m+n+p+q=3$ ). The compound represented by formula I is particularly



I



II



III

desirably one represented by formula I (wherein M is Cr) and is exemplified by one represented by formula III. The compound represented by formula II is exemplified by trimethylaluminum or diethylaluminum ethoxide. An  $\alpha$ -olefin is oligomerized in the presence of a catalyst system comprising the compounds represented by formulas I and II. More particularly, 1-hexene as a comonomer for LLDPE can be selectively produced from ethylene.

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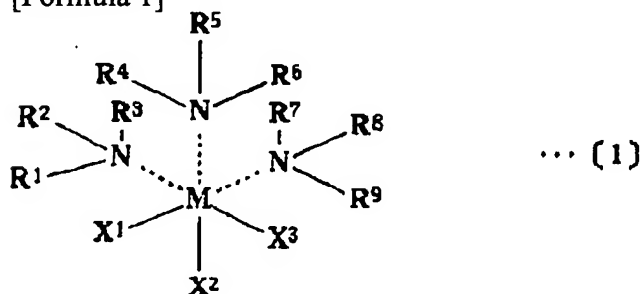
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## CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of an alpha olefin polymer including the process which makes an alpha olefin react to the bottom of existence with the transition-metals compound shown by the general formula [1], and the aluminium compound shown by the general formula [2].

[Formula 1]



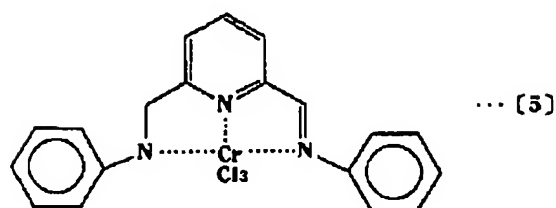
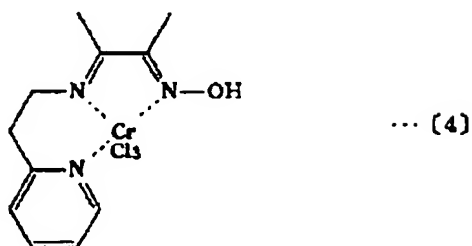
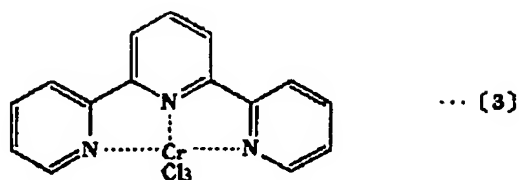
M is transition metals among [type. R1-R9, respectively A hydrogen atom, a hydroxyl group, They are the alkyl group of a straight chain or the letter of branching, an alkenyl radical, or an aryl group. You may differ, even if the same, and you may have the substituent, it may join mutually together, and a ring or bridge formation may be formed. moreover, two pieces may coalesce, the alkylidene radical, the alkenylidene radical, or the ARIRIDEN radical may be formed, and X1-X3 are the alkyl groups of a hydrogen atom, a halogen atom, a straight chain, or the letter of branching, even if they are the same, they may differ from each other, and they may have the substituent. ]

[Formula 2]  $R_{11}mAl(OR_{12})_nXpHq \dots$  [2]

R11 and R12 are the hydrocarbon groups of carbon numbers 1-15 among [type, respectively, even if the same, you may differ, and X expresses a halogen atom.  $0 < m \leq 3$  and n are [  $0 \leq p < 3$  and q of  $0 \leq n < 3$  and p ] each number of  $0 \leq q < 3$ , and m is  $m+n+p+q=3$ . ]

[Claim 2] The approach according to claim 1 of being that as which a transition-metals compound is chosen from the compound shown by formula [3]- [5].

[Formula 3]



[Claim 3] The approach according to claim 1 or 2 of being that as which an aluminium compound is chosen from general formula [6]- [9].

[Formula 4]

R113aluminum -- [6]

R11mAlX<sub>3-m</sub> (m is 1.5 ≤ m < 3) -- [7]

R11mAl(OR12)<sub>3-m</sub> (m is 0 < m < 3) -- [8]

R11mAlH<sub>3-m</sub> (m is 0 < m < 3) -- [9]

R11 and R12 are the hydrocarbon groups of carbon numbers 1-15 among [type, respectively, even if the same, you may differ, and X expresses a halogen. ]

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]**

**[0001]**

**[Field of the Invention]** This invention relates to the manufacture approach of the alpha olefin polymer suitable for manufacturing selectively 1-hexene useful as a comonomer of ethylene or spiral-like low density polyethylene (LLDPE) efficiently especially about the manufacture approach of the polymer (oligomer) of an alpha olefin.

**[0002]**

**[Description of the Prior Art]** The alpha olefin polymer for polyolefine raw materials can be manufactured by many quantifying the alpha olefin of low molecular weight comparatively. 1-hexene, 1-octene, etc. which can be manufactured by many quantifying ethylene in recent years -- a line -- it is useful as a comonomer of low density polyethylene (LLDPE), and the importance is increasing industrially. The approach of using from the former the chromium system catalyst which consists of combination of a specific chromium compound and a specific aluminium compound as the multi-quantification approach of alpha olefins, such as ethylene, is learned.

**[0003]** For example, it is expressed with a general formula  $MX_n$  to JP,43-18707,B, and the method of obtaining a hexene -1 from ethylene is describing at it by the catalyst system which consists of a VIA group's transition-metals compound (M) and poly hydrocarbonyl aluminum oxide (X) containing chromium. However, this approach has low selectivity and polyethylene carries out many byproductions to 1-hexene and coincidence. Moreover, there is a trouble that catalytic activity falls, on the conditions which pressed down the byproduction of polyethylene.

**[0004]** The method of quantifying an alpha olefin three times using the catalyst which the chromium content compound, the alkyl metal, or Lewis acid which has chromium-pyrrolyl association was made to react to JP,3-128904,A beforehand on the other hand, and was acquired is indicated. However, by this approach, there is a trouble that catalytic activity is low and many quantification cannot be performed efficiently.

**[0005]**

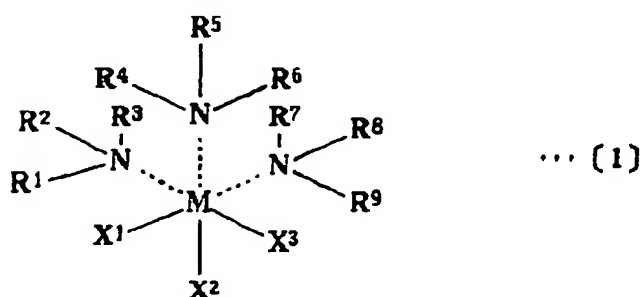
**[Problem(s) to be Solved by the Invention]** The object of this invention is proposing the manufacture approach of the alpha olefin polymer which can manufacture a specific alpha olefin polymer efficiently selectively, and can manufacture selectively 1-hexene useful as a comonomer of ethylene or spiral-like low density polyethylene (LLDPE) efficiently especially.

**[0006]**

**[Means for Solving the Problem]** This invention is the manufacture approach of the following alpha olefin polymer.

(1) The manufacture approach of an alpha olefin polymer including the process which makes an alpha olefin react to the bottom of existence with the transition-metals compound shown by the general formula [1], and the aluminium compound shown by the general formula [2].

**[Formula 5]**



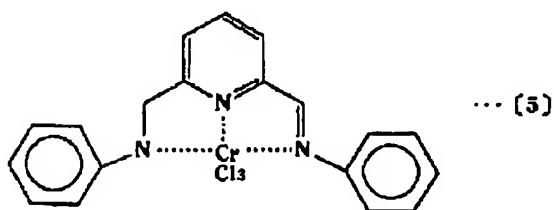
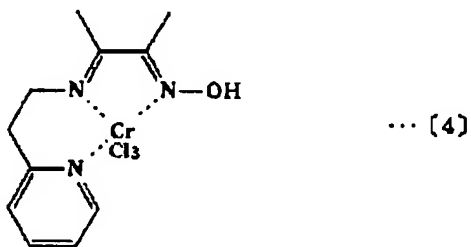
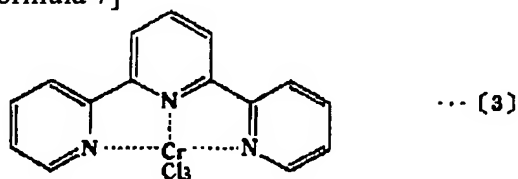
M is transition metals among [type. R1-R9, respectively A hydrogen atom, a hydroxyl group, They are the alkyl group of a straight chain or the letter of branching, an alkenyl radical, or an aryl group. You may differ, even if the same, and you may have the substituent, it may join mutually together, and a ring or bridge formation may be formed. moreover, two pieces may coalesce, the alkylidene radical, the alkenylidene radical, or the ARIRIDEN radical may be formed, and X1-X3 are the alkyl groups of a hydrogen atom, a halogen atom, a straight chain, or the letter of branching, even if they are the same, they may differ from each other, and they may have the substituent. ]

[Formula 6]  $R_{11}mAl(OR_{12})_nX_pH_q \dots [2]$

R11 and R12 are the hydrocarbon groups of carbon numbers 1-15 among [type, respectively, even if the same, you may differ, and X expresses a halogen atom.  $0 < m \leq 3$  and n are [  $0 \leq p < 3$  and q of  $0 \leq n < 3$  and p ] each number of  $0 \leq q < 3$ , and m is  $m+n+p+q=3$ . ]

(2) The approach of the above-mentioned (1) publication which is that as which a transition-metals compound is chosen from the compound shown by formula [3]- [5].

[Formula 7]



(3) An approach the above (1) which is that as which an aluminium compound is chosen from general formula [6]- [9], or given in (2).

[Formula 8]

R113aluminum -- [6]

$R_{11}mAlX_{3-m}$  (m is  $1.5 \leq m < 3$ ) -- [7]

$R_{11}mAl(OR_{12})_{3-m}$  (m is  $0 < m < 3$ ) -- [8]

$R_{11}mAlH_{3-m}$  (m is  $0 < m < 3$ ) -- [9]

R11 and R12 are the hydrocarbon groups of carbon numbers 1-15 among [type, respectively, even if the same, you may differ, and X expresses a halogen. ]

[0007] In this invention, an alpha olefin polymer (oligomer) is set as the object of manufacture, and, generally 3 - 10 \*\*\*\* is raised preferably two to 20 \*\*\*\*. As an alpha olefin used as a raw material, the permutation or the unsubstituted alpha olefin of 2-30 is used for a carbon number. Specifically, ethylene, a propylene, 1-butene, 1-hexene, 1-octene, a 3-methyl-1-butene, 4-methyl-1-pentene, etc. are raised. the approach of manufacturing especially 1-hexene which ethylene is suitable and is the trimer from ethylene as a raw material alpha olefin -- suitable -- \*\*\*\* -- high yield and high -- 1-hexene can be obtained selectively.

[0008] The catalyst used for the multi-quantification reaction of an alpha olefin in this invention is a catalyst system which consists of said transition-metals compound and aluminium compound. The compound with which a transition-metals compound is shown in said general formula [1] is used, and the compound of a general formula [2] is used as an aluminium compound.

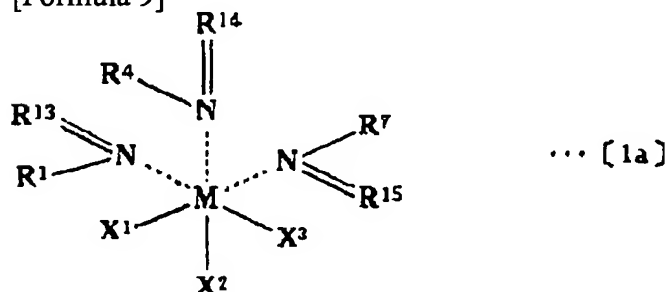
[0009] Although not limited especially as transition metals shown by M in a general formula [1], 5 - 9 group's thing is desirable, for example, vanadium, chromium, manganese, iron, cobalt, molybdenum, etc. are raised, and especially chromium is desirable. The compound of a general formula [1] is the complex of at least one sort of transition metals chosen from these. As the typical thing, a vanadium (III) complex, a chromium (III) complex, a manganese (III) complex, an iron (III) complex, a cobalt (III) complex, a molybdenum (III) complex, etc. are mentioned, and especially a chromium (III) complex is desirable.

[0010] a general formula [1] -- setting -- R1-R9 -- respectively -- a hydrogen atom, a hydroxyl group, and carbon numbers 1-15 -- desirable -- the straight chain of 1-8, or the alkyl group of the letter of branching -- Although it is an alkenyl radical or an aryl group, you may differ even if the same, and you may have the substituent, it may join mutually together and a ring or bridge formation may be formed, it is desirable for two pieces to coalesce and to form the alkylidene radical, the alkenylidene radical, or the ARIRIDEN radical.

[0011] In this case, as for the alkylidene radical which it combines each with N, an alkenylidene radical, or an ARIRIDEN radical, it is desirable to combine with R1-R9 or the alkylidene radical, alkenylidene radical, or ARIRIDEN radical combined with N which combines with R1-R9 which are combined with the same N, forms a ring and adjoins, and to form bridge formation. In the general formula [1], X1-X3 are the alkyl groups of a hydrogen atom, a halogen atom, a straight chain, or the letter of branching, respectively, even if they are the same, they may differ from each other, and they may have the substituent.

[0012] The compound of the following general formula [1a] is raised as a compound with the desirable transition-metals compound of a general formula [1].

[Formula 9]



the inside of [type, and what has M, R1, R4, R7, X1-X3 -- being shown -- R13, R14, and R15 -- carbon numbers 1-15 -- the alkylidene, the alkenylidene, or the ARIRIDEN radical of 1-8 is shown preferably, mutual may be carried out, it may join together and these may form a ring or bridge formation. ] [ the same as the above ]

[0013] As a desirable example of the transition-metals compound shown by such a general formula [1] or [2], the thing of said formula [3]- [5] is raised. The compounds of a formula [3] are alpha, alpha', and

alpha"-TORIPI lysine chromium (III) chloride, can make alpha, alpha', and an alpha"-TORIPI lysine and a chromium(III) chloride THF (tetrahydrofuran) complex able to react, and can be manufactured. The compound of a formula [4] is 2 and 6-screw (2-phenyl-2-aza-ethenyl) pyridine chromium (III) chloride, can make 2 and 6-screw (2-phenyl-2-aza-ethenyl) pyridine and a chromium(III) chloride THF complex able to react, and can be manufactured. The compound of a formula [5] is screw [3-(2-pyridyl ethylimino)-2-butanone oxime] chromium (III) chloride, can make a screw [a 3-(2-pyridyl ethylimino)-2-butanone oxime] and a chromium(III) chloride THF complex able to react, and can be manufactured. [0014] the aluminium compound shown by the general formula [2] -- setting -- R11 and R12 -- respectively -- carbon numbers 1-15 -- it is the hydrocarbon group of 1-8 preferably, and even if the same, you may differ. X shows a halogen. m, n, p, and q are the numbers of averages, and show the aforementioned value.

[0015] The compound of said general formula [6]- [9] is raised with such a general formula [2] as a desirable compound of an aluminium compound. general formula [6]- [9] -- setting -- as R11 and R12 -- carbon numbers 1-15 -- the alkyl group, alkenyl radical, or aryl group of 1-8 is preferably desirable. a general formula [8] and [9] -- setting -- m --  $0 < m < 3$  -- it is  $1.5 \leq m < 3$  preferably.

[0016] As an example of the above-mentioned aluminium compound, trimethylaluminum, triethylaluminum, triisobutylaluminum, and diethyl aluminum mono-chloride, ethyl aluminum dichloride, diethyl aluminum ethoxide, a diethyl aluminum hydride, etc. are raised.

[0017] The manufacture approach of the alpha olefin polymer of this invention performs many quantification of the alpha olefin of a raw material in a solvent using the catalyst system which consists of each above-mentioned catalyst component, and collects polymers. Usually let preferably the 1x10<sup>-4</sup>-5g of the amount of the transition-metals compound used be the range of 1x10<sup>-3</sup>-1g per solvent 1 liter. the amount of the aluminium compound used -- per 1g of transition-metals compounds -- usually -- 0.01mmol(s)- preferably is taken for the range of 0.1mmol(s) - 1000mmol 10000 mmol.

[0018] As a solvent, chlorinated aromatic hydrocarbon, such as chain-like chlorinated hydrocarbons, such as aromatic hydrocarbon, such as saturated hydrocarbon the shape of a straight chain, such as a pentane, a hexane, a cyclohexane, a methylcyclohexane, a heptane, an octane, and a decalin, and alicyclic, benzene, toluene, ethylbenzene, a xylene, a mesitylene, and a tetralin, dichloromethane, chloroform, and a carbon-tetrachloride dichloroethane, a chlorobenzene, and a dichlorobenzene, etc. is used. these are independent -- it is -- it can be used as a mixed solvent. Since catalytic activity with expensive aromatic hydrocarbon, such as benzene, toluene, ethylbenzene, a xylene, a mesitylene, and a tetralin, is acquired especially, it is suitable.

[0019] Usually let preferably 0-160 degrees C of reaction temperature be the range of 50-150 degrees C. reaction pressure -- ordinary pressure thru/or 200 kg/cm<sup>2</sup> -- let 5-100kg /be the range of 2 cm preferably. Especially reaction time is not limited but can be set up suitably. In this invention, especially the method of contact of a transition-metals compound and an aluminium compound, and a raw material alpha olefin cannot be limited, but can make a multi-quantification reaction able to perform selectively, and can manufacture a polymer selectively from a raw material alpha olefin.

[0020]

[Embodiment of the Invention] Hereafter, the example of this invention is explained.

[0021] Example 1 of reference Composition alpha and alpha', and alpha"alpha [ which - TORIPI lysine 0.5g (2.1mmol), 1.0g (2.7mmol) of chromium(III) chloride THF complexes, and 30ml of methylene chlorides are stirred at a room temperature under an argon ambient atmosphere for 3 hours, and the depositing crystal is filtered, and is the compound of a formula [3] ], alpha', alpha"-TORIPI lysine chromium (III) chloride 0.68g was obtained (83% of yield). [ of the compound of a formula [3] ] The result of the FD mass spectrometry is shown below.

FD-MS 390(M+)

[0022] Example 2 of reference Pyridine -2 and 6-carboxy aldehyde 3.0g (22.2mmol), aniline 5.0g (53.4mmol), and methanol 100ml were put into the 200ml container equipped with synthetic stirring and reflux equipment of the compound of a formula [4] under nitrogen-gas-atmosphere mind, and stirring was performed at 50 degrees C for 8 hours. After cooling radiationally, the produced crystal was filtered

and 2 and 6-screw (2-phenyl-2-aza-ethenyl) pyridine 3.1g was obtained (49% of yield). The result of the <sup>1</sup>HNMR is shown below.

<sup>1</sup>HNMR (CDCl<sub>3</sub>, delta, ppm)

7.20-7.60(m,10H)

8.01(d,1H,9.0Hz)

8.32(d,2H,9.0Hz)

8.76(s,2H)

[0023] Obtained 2 and 6-screw (2-phenyl-2-aza-ethenyl) pyridine 0.6g (2.1mmol), 1.0g (2.7mmol) of chromium(III) chloride THF complexes, and 30ml of methylene chlorides were stirred at the room temperature under the argon ambient atmosphere for 3 hours, the depositing crystal was filtered, and 2 and 6-screw (2-phenyl-2-aza-ethenyl) pyridine chromium (III) chloride 0.85g which is the compound of a formula [4] was obtained (72% of yield). The result of analysis of the FD mass spectrum is shown below.

FD-MS 442(M<sup>+</sup>)

[0024] Example 3 of reference Synthetic screw [3-(2-pyridyl ethylimino)-2-butanone oxime] 440mg (2.1mmol) and dichloromethane 20ml of a compound of a formula [5] were stirred under the argon ambient atmosphere, and 10ml of 800mg (2.1mmol) dichloromethane solutions of chromium(III) chloride THF complexes was dropped. After stirring at a room temperature for 3 hours, the depositing crystal was filtered, it was made to dry and 530mg of green crystals of the screw [3-(2-pyridyl ethylimino)-2-butanone oxime] chromium (III) chloride which is the compound of a formula [5] was obtained (69% of yield).

[0025] After assembling the 50 cc autoclave which carried out example 1 stoving in the state of heating, the vacuum nitrogen purge was carried out. Compound [ of the formula [3] obtained in the example 1 of reference ] (0.50mmol), triethylaluminum (5.0mmol), and toluene 10ml was added to this autoclave under nitrogen-gas-atmosphere mind, ethylene was introduced until the total pressure of ethylene became 30 kg/cm<sup>2</sup>, and temperature was maintained at 130 degrees C. Ethanol was added 1 hour after and into the autoclave, and the reaction was suspended. The pressure of an autoclave was canceled, degasifying was performed and the gas chromatography performed gas analysis. The gas chromatography also performed analysis of the product in reaction mixture. As a result of observing the internal surface of an autoclave in this example, adhesion of a byproduction polymer was not accepted. The result of the component analysis of the alpha olefin polymer by the gas chromatography was shown in a table 1.

[0026] As examples 2-3 and example of comparison 1 example 1 were shown in a table 1, reaction actuation was performed like the example 1 except having changed the class of catalyst. The result of the component analysis of the alpha olefin polymer by the gas chromatography was shown in a table 1. As a result of observing the internal surface of an autoclave in examples 2-3, adhesion of a byproduction polymer was not accepted. In the case of the example 1 of a comparison, byproduction polymer adhesion was accepted.

[0027]

[A table 1]



表 1

	触 媒	選択率 (%)		触媒活性* (ターンオーバー)
		ヘキセン	その他	
実施例 1	式〔3〕	77	23	11
実施例 2	式〔4〕	59	41	128
実施例 3	式〔5〕	42	58	6
比較例 1	CrCl <sub>3</sub>	9	91	330

\* From the amount of oligomer generation, it is calculation [0028] at ethylene \*\*.

[Effect of the Invention] the case where according to this invention can manufacture a specific alpha olefin polymer efficiently selectively, and ethylene is used especially as an alpha olefin by using a specific catalyst -- a line -- 1-hexene useful, as a comonomer of low density polyethylene (LLDPE) can be manufactured efficiently selectively.

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PRIOR ART

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[Description of the Prior Art] The alpha olefin polymer for polyolefine raw materials can be manufactured by many quantifying the alpha olefin of low molecular weight comparatively. 1-hexene, 1-octene, etc. which can be manufactured by many quantifying ethylene in recent years -- a line -- it is useful as a comonomer of low density polyethylene (LLDPE), and the importance is increasing industrially. The approach of using from the former the chromium system catalyst which consists of combination of a specific chromium compound and a specific aluminium compound as the multi-quantification approach of alpha olefins, such as ethylene, is learned.

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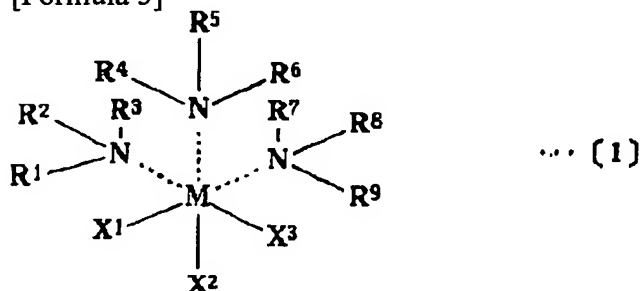
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## MEANS

[Means for Solving the Problem] This invention is the manufacture approach of the following alpha olefin polymer.

(1) The manufacture approach of an alpha olefin polymer including the process which makes an alpha olefin react to the bottom of existence with the transition-metals compound shown by the general formula [1], and the aluminium compound shown by the general formula [2].

[Formula 5]



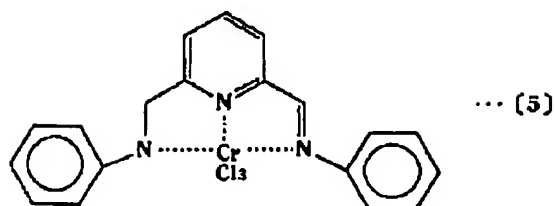
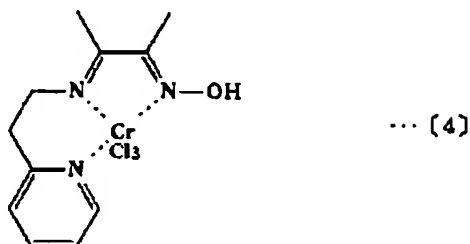
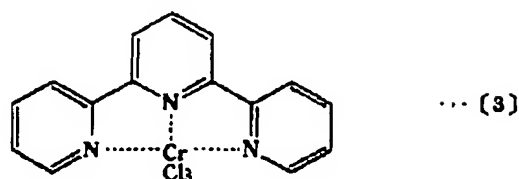
M is transition metals among [type. R1-R9, respectively A hydrogen atom, a hydroxyl group, They are the alkyl group of a straight chain or the letter of branching, an alkenyl radical, or an aryl group. You may differ, even if the same, and you may have the substituent, it may join mutually together, and a ring or bridge formation may be formed. moreover, two pieces may coalesce, the alkylidene radical, the alkenylidene radical, or the ARIRIDEN radical may be formed, and X1-X3 are the alkyl groups of a hydrogen atom, a halogen atom, a straight chain, or the letter of branching, even if they are the same, they may differ from each other, and they may have the substituent. ]

[Formula 6]  $R_{11}mAl(OR_{12})_nX_pH_q$  ... [2]

R11 and R12 are the hydrocarbon groups of carbon numbers 1-15 among [type, respectively, even if the same, you may differ, and X expresses a halogen atom.  $0 < m \leq 3$  and n are [  $0 \leq p < 3$  and q of  $0 \leq n < 3$  and p ] each number of  $0 \leq q < 3$ , and m is  $m+n+p+q=3$ . ]

(2) The approach of the above-mentioned (1) publication which is that as which a transition-metals compound is chosen from the compound shown by formula [3]- [5].

[Formula 7]



(3) An approach the above (1) which is that as which an aluminium compound is chosen from general formula [6]- [9], or given in (2).

[Formula 8]

R113aluminum -- [6]

R11mAlX<sub>3-m</sub> (m is 1.5 ≤ m < 3) -- [7]

R11mAl(OR<sub>12</sub>)<sub>3-m</sub> (m is 0 < m < 3) -- [8]

R11mAlH<sub>3-m</sub> (m is 0 < m < 3) -- [9]

R11 and R12 are the hydrocarbon groups of carbon numbers 1-15 among [type, respectively, even if the same, you may differ, and X expresses a halogen. ]

[0007] In this invention, an alpha olefin polymer (oligomer) is set as the object of manufacture, and, generally 3 - 10 \*\*\*\* is raised preferably two to 20 \*\*\*\*. As an alpha olefin used as a raw material, the permutation or the unsubstituted alpha olefin of 2-30 is used for a carbon number. Specifically, ethylene, a propylene, 1-butene, 1-hexene, 1-octene, a 3-methyl-1-butene, 4-methyl-1-pentene, etc. are raised. the approach of manufacturing especially 1-hexene which ethylene is suitable and is the trimer from ethylene as a raw material alpha olefin -- suitable -- \*\*\*\* -- high yield and high -- 1-hexene can be obtained selectively.

[0008] The catalyst used for the multi-quantification reaction of an alpha olefin in this invention is a catalyst system which consists of said transition-metals compound and aluminium compound. The compound with which a transition-metals compound is shown in said general formula [1] is used, and the compound of a general formula [2] is used as an aluminium compound.

[0009] Although not limited especially as transition metals shown by M in a general formula [1], 5 - 9 group's thing is desirable, for example, vanadium, chromium, manganese, iron, cobalt, molybdenum, etc. are raised, and especially chromium is desirable. The compound of a general formula [1] is the complex of at least one sort of transition metals chosen from these. As the typical thing, a vanadium (III) complex, a chromium (III) complex, a manganese (III) complex, an iron (III) complex, a cobalt (III) complex, a molybdenum (III) complex, etc. are mentioned, and especially a chromium (III) complex is desirable.

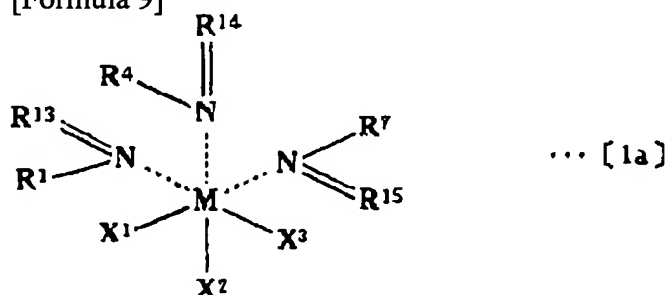
[0010] a general formula [1] -- setting -- R1-R9 -- respectively -- a hydrogen atom, a hydroxyl group, and carbon numbers 1-15 -- desirable -- the straight chain of 1-8, or the alkyl group of the letter of branching -- Although it is an alkenyl radical or an aryl group, you may differ even if the same, and you

may have the substituent, it may join mutually together and a ring or bridge formation may be formed, it is desirable for two pieces to coalesce and to form the alkylidene radical, the alkenylidene radical, or the ARIRIDEN radical.

[0011] In this case, as for the alkylidene radical which it combines each with N, an alkenylidene radical, or an ARIRIDEN radical, it is desirable to combine with R1-R9 or the alkylidene radical, alkenylidene radical, or ARIRIDEN radical combined with N which combines with R1-R9 which are combined with the same N, forms a ring and adjoins, and to form bridge formation. In the general formula [1], X1-X3 are the alkyl groups of a hydrogen atom, a halogen atom, a straight chain, or the letter of branching, respectively, even if they are the same, they may differ from each other, and they may have the substituent.

[0012] The compound of the following general formula [1a] is raised as a compound with the desirable transition-metals compound of a general formula [1].

[Formula 9]



the inside of [type, and what has M, R1, R4, R7, X1-X3 -- being shown -- R13, R14, and R15 -- carbon numbers 1-15 -- the alkylidene, the alkenylidene, or the ARIRIDEN radical of 1-8 is shown preferably, mutual may be carried out, it may join together and these may form a ring or bridge formation. ] [ the same as the above ]

[0013] As a desirable example of the transition-metals compound shown by such a general formula [1] or [2], the thing of said formula [3]- [5] is raised. The compounds of a formula [3] are alpha, alpha', and alpha"-TORIPI lysine chromium (III) chloride, can make alpha, alpha', and an alpha"-TORIPI lysine and a chromium(III) chloride THF (tetrahydrofuran) complex able to react, and can be manufactured. The compound of a formula [4] is 2 and 6-screw (2-phenyl-2-aza-ethenyl) pyridine chromium (III) chloride, can make 2 and 6-screw (2-phenyl-2-aza-ethenyl) pyridine and a chromium(III) chloride THF complex able to react, and can be manufactured. The compound of a formula [5] is screw [3-(2-pyridyl ethylimino)-2-butanone oxime] chromium (III) chloride, can make a screw [a 3-(2-pyridyl ethylimino)-2-butanone oxime] and a chromium(III) chloride THF complex able to react, and can be manufactured.

[0014] the aluminium compound shown by the general formula [2] -- setting -- R11 and R12 -- respectively -- carbon numbers 1-15 -- it is the hydrocarbon group of 1-8 preferably, and even if the same, you may differ. X shows a halogen. m, n, p, and q are the numbers of averages, and show the aforementioned value.

[0015] The compound of said general formula [6]- [9] is raised with such a general formula [2] as a desirable compound of an aluminium compound. general formula [6]- [9] -- setting -- as R11 and R12 -- carbon numbers 1-15 -- the alkyl group, alkenyl radical, or aryl group of 1-8 is preferably desirable. a general formula [8] and [9] -- setting -- m --  $0 < m < 3$  -- it is  $1.5 \leq m < 3$  preferably.

[0016] As an example of the above-mentioned aluminium compound, trimethylaluminum, triethylaluminum, triisobutylaluminum, and diethyl aluminum mono-chloride, ethyl aluminum dichloride, diethyl aluminum ethoxide, a diethyl aluminum hydride, etc. are raised.

[0017] The manufacture approach of the alpha olefin polymer of this invention performs many quantification of the alpha olefin of a raw material in a solvent using the catalyst system which consists of each above-mentioned catalyst component, and collects polymers. Usually let preferably the  $1 \times 10^{-4}$ -5g of the amount of the transition-metals compound used be the range of  $1 \times 10^{-3}$ -1g per solvent 1 liter. the amount of the aluminium compound used -- per 1g of transition-metals compounds -- usually --

0.01mmol(s)- preferably is taken for the range of 0.1mmol(s) - 1000mmol 10000 mmol.

[0018] As a solvent, chlorinated aromatic hydrocarbon, such as chain-like chlorinated hydrocarbons, such as aromatic hydrocarbon, such as saturated hydrocarbon the shape of a straight chain, such as a pentane, a hexane, a cyclohexane, a methylcyclohexane, a heptane, an octane, and a decalin, and alicyclic, benzene, toluene, ethylbenzene, a xylene, a mesitylene, and a tetralin, dichloromethane, chloroform, and a carbon-tetrachloride dichloroethane, a chlorobenzene, and a dichlorobenzene, etc. is used. these are independent -- it is -- it can be used as a mixed solvent. Since catalytic activity with expensive aromatic hydrocarbon, such as benzene, toluene, ethylbenzene, a xylene, a mesitylene, and a tetralin, is acquired especially, it is suitable.

[0019] Usually let preferably 0-160 degrees C of reaction temperature be the range of 50-150 degrees C. reaction pressure -- ordinary pressure thru/or 200 kg/cm<sup>2</sup> -- let 5-100kg /be the range of 2 cm preferably. Especially reaction time is not limited but can be set up suitably. In this invention, especially the method of contact of a transition-metals compound and an aluminium compound, and a raw material alpha olefin cannot be limited, but can make a multi-quantification reaction able to perform selectively, and can manufacture a polymer selectively from a raw material alpha olefin.

[0020]

[Embodiment of the Invention] Hereafter, the example of this invention is explained.

[0021] Example 1 of reference Composition alpha and alpha', and alpha"alpha [ which - TORIPI lysine 0.5g (2.1mmol), 1.0g (2.7mmol) of chromium(III) chloride THF complexes, and 30ml of methylene chlorides are stirred at a room temperature under an argon ambient atmosphere for 3 hours, and the depositing crystal is filtered, and is the compound of a formula [3] ], alpha', alpha"-TORIPI lysine chromium (III) chloride 0.68g was obtained (83% of yield). [ of the compound of a formula [3] ] The result of the FD mass spectrometry is shown below.

FD-MS 390(M+)

[0022] Example 2 of reference Pyridine -2 and 6-carboxy aldehyde 3.0g (22.2mmol), aniline 5.0g (53.4mmol), and methanol 100ml were put into the 200ml container equipped with synthetic stirring and reflux equipment of the compound of a formula [4] under nitrogen-gas-atmosphere mind, and stirring was performed at 50 degrees C for 8 hours. After cooling radiationally, the produced crystal was filtered and 2 and 6-screw (2-phenyl-2-aza-ethenyl) pyridine 3.1g was obtained (49% of yield). The result of the <sup>1</sup>HNMR is shown below.

<sup>1</sup>HNMR (CDCl<sub>3</sub>, delta, ppm)

7.20-7.60(m,10H)

8.01(d,1H,9.0Hz)

8.32(d,2H,9.0Hz)

8.76(s,2H)

[0023] Obtained 2 and 6-screw (2-phenyl-2-aza-ethenyl) pyridine 0.6g (2.1mmol), 1.0g (2.7mmol) of chromium(III) chloride THF complexes, and 30ml of methylene chlorides were stirred at the room temperature under the argon ambient atmosphere for 3 hours, the depositing crystal was filtered, and 2 and 6-screw (2-phenyl-2-aza-ethenyl) pyridine chromium (III) chloride 0.85g which is the compound of a formula [4] was obtained (72% of yield). The result of analysis of the FD mass spectrum is shown below.

FD-MS 442(M+)

[0024] Example 3 of reference Synthetic screw [3-(2-pyridyl ethylimino)-2-butanone oxime] 440mg (2.1mmol) and dichloromethane 20ml of a compound of a formula [5] were stirred under the argon ambient atmosphere, and 10ml of 800mg (2.1mmol) dichloromethane solutions of chromium(III) chloride THF complexes was dropped. After stirring at a room temperature for 3 hours, the depositing crystal was filtered, it was made to dry and 530mg of green crystals of the screw [3-(2-pyridyl ethylimino)-2-butanone oxime] chromium (III) chloride which is the compound of a formula [5] was obtained (69% of yield).

[0025] After assembling the 50 cc autoclave which carried out example 1 stoving in the state of heating, the vacuum nitrogen purge was carried out. Compound [ of the formula [3] obtained in the example 1 of

reference ] (0.50mmol), triethylaluminum (5.0mmol), and toluene 10ml was added to this autoclave under nitrogen-gas-atmosphere mind, ethylene was introduced until the total pressure of ethylene became 30 kg/cm<sup>2</sup>, and temperature was maintained at 130 degrees C. Ethanol was added 1 hour after and into the autoclave, and the reaction was suspended. The pressure of an autoclave was canceled, degasifying was performed and the gas chromatography performed gas analysis. The gas chromatography also performed analysis of the product in reaction mixture. As a result of observing the internal surface of an autoclave in this example, adhesion of a byproduction polymer was not accepted. The result of the component analysis of the alpha olefin polymer by the gas chromatography was shown in a table 1.

[0026] As examples 2-3 and example of comparison 1 example 1 were shown in a table 1, reaction actuation was performed like the example 1 except having changed the class of catalyst. The result of the component analysis of the alpha olefin polymer by the gas chromatography was shown in a table 1. As a result of observing the internal surface of an autoclave in examples 2-3, adhesion of a byproduction polymer was not accepted. In the case of the example 1 of a comparison, byproduction polymer adhesion was accepted.

[0027]

[A table 1]

表 1

	触 媒	選択率 (%)		触媒活性* (ターンオーバー)
		ヘキセン	その他	
実施例 1	式〔3〕	7 7	2 3	1 1
実施例 2	式〔4〕	5 9	4 1	1 2 8
実施例 3	式〔5〕	4 2	5 8	6
比較例 1	C r C l <sub>3</sub>	9	9 1	3 3 0

\* Compute by ethylene \*\* from the amount of oligomer generation.

[Translation done.]

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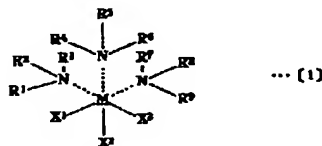
(54)【発明の名称】  $\alpha$ -オレフィン多量体の製造方法

(57)【要約】

【課題】 特定の触媒を用いることにより、特定の $\alpha$ -オレフィン多量体を選択的に効率よく製造でき、特に $\alpha$ -オレフィンとしてエチレンを用いる場合、線状低密度ポリエチレン(LLDPE)のコモノマーとして有用な1-ヘキセンを選択的に効率よく製造することができる $\alpha$ -オレフィン多量体の製造方法を得る。

【解決手段】 一般式〔1〕で示される遷移金属化合物と、一般式〔2〕で示されるアルミニウム化合物との存在下に $\alpha$ -オレフィンを反応させる工程を含む $\alpha$ -オレフィン多量体の製造方法。

【化1】



〔式中、Mは遷移金属であり、R<sup>1</sup>~R<sup>6</sup>はそれぞれ水素原子、水酸基、直鎖または分岐状のアルキル基、アルケニル基もしくはアリール基であって同一でも異なってもよく、置換基を有していてもよく、相互に結合して環または架橋を形成していてもよく、また2個が合体してアルキリデン基、アルケニリデン基もしくはアリーリデン基を形成していてもよく、X<sup>1</sup>~X<sup>2</sup>は水素原子、ハロゲン原子、直鎖または分岐状のアルキル基であって同一でも異なってもよく、置換基を有していてもよい。〕



〔式中、R<sup>11</sup>、R<sup>12</sup>はそれぞれ炭素数1~15の炭化水素基であり、同一でも異なってもよく、Xはハロゲン原子を表す。mは0<m≤3、nは0≤n<3、pは0≤p<3、qは0≤q<3のそれぞれの数であり、m+n+p+q=3である。〕



1

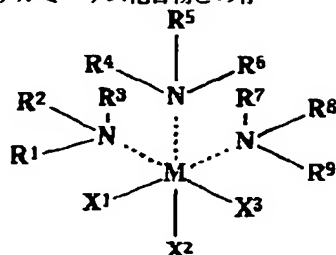
2

【特許請求の範囲】

【請求項1】 一般式〔1〕で示される遷移金属化合物と、一般式〔2〕で示されるアルミニウム化合物との存\*

\*在下に、 $\alpha$ -オレフィンを反応させる工程を含む $\alpha$ -オレフィン多量体の製造方法。

【化1】



…〔1〕

〔式中、Mは遷移金属であり、R<sup>1</sup>～R<sup>9</sup>はそれぞれ水素原子、水酸基、直鎖または分岐状のアルキル基、アルケニル基もしくはアリール基であって、同一でも異なってもよく、置換基を有していてもよく、相互に結合して環または架橋を形成していてもよく、また2個が合体してアルキリデン基、アルケニリデン基もしくはアリールリデン基を形成していてもよく、X<sup>1</sup>～X<sup>3</sup>は水素原子、ハロゲン原子、直鎖または分岐状のアルキル基であって同一でも異なってもよく、置換基を有していてもよい。〕

※【請求項3】 アルミニウム化合物が一般式〔6〕～〔9〕から選ばれるものである請求項1または2記載の方法。

【化4】

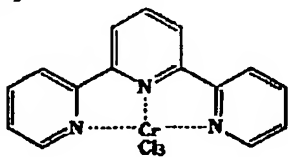
【化2】 R<sup>11</sup><sub>m</sub>Al(OR<sup>12</sup>)<sub>n</sub>X<sub>p</sub>H<sub>q</sub> …〔2〕

〔式中、R<sup>11</sup>、R<sup>12</sup>はそれぞれ炭素数1～15の炭化水素基であり、同一でも異なってもよく、Xはハロゲン原子を表す。mは0<m≤3、nは0≤n<3、pは0≤p<3、qは0≤q<3のそれぞれの数であり、m+n+p+q=3である。〕

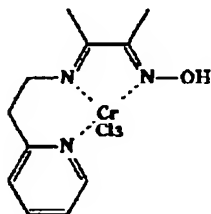
【請求項2】 遷移金属化合物が式〔3〕～〔5〕で示される化合物から選ばれるものである請求項1記載の方法。

30

【化3】

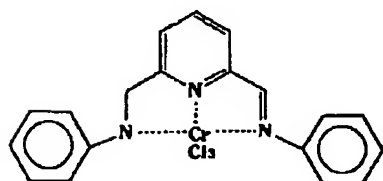


…〔3〕



…〔4〕

40



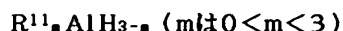
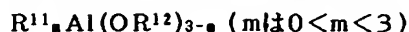
…〔5〕

※

R<sup>11</sup><sub>3</sub>Al

…〔6〕

3



〔式中、 $R^{11}$ 、 $R^{12}$ はそれぞれ炭素数1～15の炭化水素基であり、同一でも異なってもよく、Xはハロゲンを表す。〕

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、 $\alpha$ -オレフィンの多量体（オリゴマー）の製造方法に関し、特にエチレンから線状低密度ポリエチレン（LLDPE）のコモノマーとして有用な1-ヘキセンを選択的に効率よく製造するのに適した $\alpha$ -オレフィン多量体の製造方法に関する。

【0002】

【従来の技術】ポリオレフィン原料用の $\alpha$ -オレフィン多量体は、比較的分子量の $\alpha$ -オレフィンを多量化することによって製造できる。近年、エチレンを多量化することによって製造できる1-ヘキセン、1-オクテンなどは、線状低密度ポリエチレン（LLDPE）のコモノマーとして有用であり、工業的にその重要性が増している。従来からエチレン等の $\alpha$ -オレフィンの多量化方法として、特定のクロム化合物と特定のアルミニウム化合物の組み合わせからなるクロム系触媒を使用する方法が知られている。

【0003】例えば、特公昭43-18707号公報には、一般式 $MX_n$ で表され、クロムを含むVIA族の遷移金属化合物（M）とポリヒドロカルビルアルミニウムオキシド（X）からなる触媒系により、エチレンからヘ\*

4

…〔7〕

…〔8〕

…〔9〕

\*キセン-1を得る方法が記されている。しかしこの方法は選択性が低く、1-ヘキセンと同時にポリエチレンが多く副生する。またポリエチレンの副生を押さえた条件では、触媒活性が低下するという問題点がある。

【0004】一方、特開平3-128904号公報には、クロム-ピロリル結合を有するクロム含有化合物とアルキル金属またはレイス酸とをあらかじめ反応させて得られた触媒を使用して $\alpha$ -オレフィンを三量化する方法が記載されている。しかしこの方法では、触媒活性が低く、効率よく多量化を行うことができないという問題点がある。

【0005】

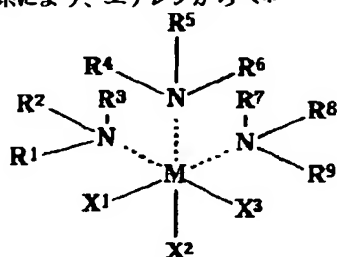
【発明が解決しようとする課題】本発明の目的は、特定の $\alpha$ -オレフィン多量体を選択的に効率よく製造することができ、特にエチレンから線状低密度ポリエチレン（LLDPE）のコモノマーとして有用な1-ヘキセンを選択的に効率よく製造することができる $\alpha$ -オレフィン多量体の製造方法を提案することである。

【0006】

【課題を解決するための手段】本発明は次の $\alpha$ -オレフィン多量体の製造方法である。

（1）一般式〔1〕で示される遷移金属化合物と、一般式〔2〕で示されるアルミニウム化合物との存在下に、 $\alpha$ -オレフィンを反応させる工程を含む $\alpha$ -オレフィン多量体の製造方法。

〔化5〕



…〔1〕

〔式中、Mは遷移金属であり、 $R^1 \sim R^9$ はそれぞれ水素原子、水酸基、直鎖または分岐状のアルキル基、アルケニル基もしくはアリール基であって、同一でも異なってもよく、置換基を有していてもよく、相互に結合して環または架橋を形成していてもよく、また2個が合体してアルキリデン基、アルケニリデン基もしくはアリリデン基を形成していてもよく、 $X^1 \sim X^3$ は水素原子、ハロゲン原子、直鎖または分岐状のアルキル基であって同一でも異なってもよく、置換基を有していてもよい。〕

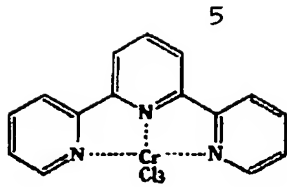
〔化6〕 $R^{11}_m Al(OR^{12})_n X_p H_q$  …〔2〕

〔式中、 $R^{11}$ 、 $R^{12}$ はそれぞれ炭素数1～15の炭化水素基であり、同一でも異なってもよく、Xはハロゲ※50

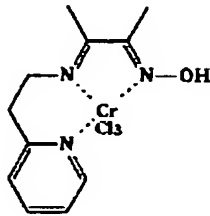
※N原子を表す。 $m$ は $0 < m \leq 3$ 、 $n$ は $0 \leq n < 3$ 、 $p$ は $0 \leq p < 3$ 、 $q$ は $0 \leq q < 3$ のそれぞれの数であり、 $m + n + p + q = 3$ である。〕

（2）遷移金属化合物が式〔3〕～〔5〕で示される化合物から選ばれるものである上記（1）記載の方法。

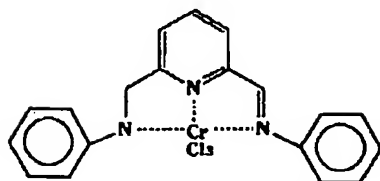
〔化7〕



... [3]



... [4]



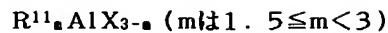
... [5]

10

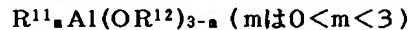
\*



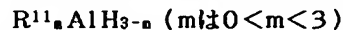
... [6]



... [7]



... [8]



... [9]

〔式中、 $R^{11}$ 、 $R^{12}$ はそれぞれ炭素数1～15の炭化水素基であり、同一でも異なっていてもよく、Xはハロゲンを表す。〕

【0007】本発明において製造の対象となるのは $\alpha$ -オレフィン多量体（オリゴマー）であり、一般的には2～20量体、好ましくは3～10量体があげられる。原料となる $\alpha$ -オレフィンとしては、炭素数が2～30の置換または非置換の $\alpha$ -オレフィンが使用される。具体的には、エチレン、プロピレン、1-ブテン、1-ヘキセン、1-オクテン、3-メチル-1-ブテン、4-メチル-1-ペンテン等があげられる。特に、原料 $\alpha$ -オレフィンとしてエチレンが好適であり、エチレンからその三量体である1-ヘキセンを製造する方法に適しており、高収率かつ高選択的に1-ヘキセンを得ることができる。

【0008】本発明において $\alpha$ -オレフィンの多量化反応に用いる触媒は前記遷移金属化合物とアルミニウム化合物からなる触媒系である。遷移金属化合物は前記一般式〔1〕に示される化合物が使用され、アルミニウム化合物としては一般式〔2〕の化合物が使用される。

【0009】一般式〔1〕においてMで示される遷移金属としては特に限定されないが5～9族のものが好ましく、例えばバナジウム、クロム、マンガン、鉄、コバルト、モリブデンなどがあげられ、特にクロムが好ましい。一般式〔1〕の化合物はこれらから選ばれる少なくとも1種の遷移金属の錯体である。その代表的なものと※

\* (3) アルミニウム化合物が一般式〔6〕～〔9〕から選ばれるものである上記(1)または(2)記載の方法。

【化8】

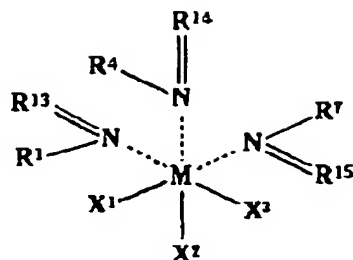
※しては、バナジウム(III)錯体、クロム(III)錯体、マンガン(III)錯体、鉄(III)錯体、コバルト(II)錯体、及びモリブデン(III)錯体等が挙げられ、特にクロム(III)錯体が好ましい。

【0010】一般式〔1〕において、 $R^1 \sim R^9$ はそれぞれ水素原子、水酸基、炭素数1～15、好ましくは1～8の直鎖または分岐状のアルキル基、アルケニル基もしくはアリール基であって、同一でも異なっていてもよく、置換基を有していてもよく、相互に結合して環または架橋を形成していてもよいが、2個が合体してアルキリデン基、アルケニリデン基もしくはアリーリデン基を形成しているのが好ましい。

【0011】この場合、各Nに結合するアルキリデン基、アルケニリデン基、もしくはアリーリデン基は、同じNに結合する $R^1 \sim R^9$ と結合して環を形成したり、また隣接するNに結合する $R^1 \sim R^9$ またはアルキリデン基、アルケニリデン基もしくはアリーリデン基と結合して架橋を形成しているのが好ましい。一般式〔1〕において、 $X^1 \sim X^3$ はそれぞれ水素原子、ハロゲン原子、直鎖または分岐状のアルキル基であって、同一でも異なっていてもよく、置換基を有していてもよい。

【0012】一般式〔1〕の遷移金属化合物の好ましい化合物として次の一般式〔1a〕の化合物があげられる。

【化9】



... [1a]

〔式中、M、R<sup>1</sup>、R<sup>4</sup>、R<sup>7</sup>、X<sup>1</sup>～X<sup>3</sup>は前記と同じものを示し、R<sup>13</sup>、R<sup>14</sup>、R<sup>15</sup>は炭素数1～15、好ましくは1～8のアルキリデン、アルケニリデンまたはアリーリデン基を示し、これらは相互して結合して環または架橋を形成していてもよい。〕

【0013】このような一般式〔1〕または〔2〕で示される遷移金属化合物の好ましい例として、前記式〔3〕～〔5〕のものがあげられる。式〔3〕の化合物は $\alpha$ 、 $\alpha'$ 、 $\alpha''$ -トリピリジクロム(III)クロリドであり、 $\alpha$ 、 $\alpha'$ 、 $\alpha''$ -トリピリジンと塩化クロム(III) THF(テトラヒドロフラン)錯体とを反応させて製造することができる。式〔4〕の化合物は2、6-ビス(2-フェニル-2-アザエチニル)ピリジクロム(III)クロリドであり、2、6-ビス(2-フェニル-2-アザエチニル)ピリジンと塩化クロム(II) THF錯体とを反応させて製造することができる。式〔5〕の化合物はビス〔3-(2-ピリジルエチルイミノ)-2-ブタノンオキシム〕クロム(III)クロリドであり、ビス〔3-(2-ピリジルエチルイミノ)-2-ブタノンオキシム〕と三塩化クロムTHF錯体とを反応させて製造することができる。

【0014】一般式〔2〕で示されるアルミニウム化合物において、R<sup>11</sup>、R<sup>12</sup>はそれぞれ炭素数1～15、好ましくは1～8の炭化水素基であり、同一でも異なってもよい。Xはハロゲンを示す。m、n、p、qは平均数であって、前記の値を示す。

【0015】このような一般式〔2〕でアルミニウム化合物の好ましい化合物として、前記一般式〔6〕～〔9〕の化合物があげられる。一般式〔6〕～〔9〕においてR<sup>11</sup>、R<sup>12</sup>としては炭素数1～15、好ましくは1～8のアルキル基、アルケニル基またはアリール基が好ましい。一般式〔8〕、〔9〕において、mは0<m<3、好ましくは1.5≤m<3である。

【0016】上記のアルミニウム化合物の具体例として、トリメチルアルミニウム、トリエチルアルミニウム、トリイソブチルアルミニウム、ジエチルアルミニウムモノクロリド、エチルアルミニウムジクロリド、ジエチルアルミニウムエトキシド、ジエチルアルミニウムヒドリド等があげられる。

【0017】本発明の $\alpha$ -オレフィン多量体の製造方法は、上記各触媒成分からなる触媒系を使用して溶媒中で原料の $\alpha$ -オレフィンの多量化を行い、多量体を回収す\* 50

\*る。遷移金属化合物の使用量は、溶媒1 liter当たり、通常 $1 \times 10^{-4}$ ～5 g、好ましくは $1 \times 10^{-3}$ ～1 gの範囲とされる。アルミニウム化合物の使用量は、遷移金属化合物1 g当たり、通常0.01 mmol～1000 mmol、好ましくは0.1 mmol～1000 mmolの範囲とされる。

【0018】溶媒としてはペンタン、ヘキサン、シクロヘキサン、メチルシクロヘキサン、ヘプタン、オクタン、デカリン等の直鎖状または脂環式の飽和炭化水素、ベンゼン、トルエン、エチルベンゼン、キシレン、メシチレン、テトラリン等の芳香族炭化水素、ジクロロメタン、クロロホルム、四塩化炭素ジクロロエタン等の鎖状塩素化炭化水素、クロロベンゼン、ジクロロベンゼン等の塩素化芳香族炭化水素等が使用される。これらは単独であるいは混合溶媒として使用することができる。特にベンゼン、トルエン、エチルベンゼン、キシレン、メシチレン、テトラリン等の芳香族炭化水素が高い触媒活性が得られるため好適である。

【0019】反応温度は、通常0～160℃、好ましくは50～150℃の範囲とされる。反応圧力は常圧ないし200 Kg/cm<sup>2</sup>、好ましくは5～100 Kg/cm<sup>2</sup>の範囲とされる。反応時間は特に限定されず、適宜設定できる。本発明において、遷移金属化合物およびアルミニウム化合物と原料 $\alpha$ -オレフィンの接触の仕方は特に限定されず、選択的に多量化反応を行わせることができ、原料 $\alpha$ -オレフィンから多量体を選択的に製造することができる。

【0020】

【発明の実施の形態】以下、本発明の実施例について説明する。

【0021】参考例1 式〔3〕の化合物の合成

$\alpha$ 、 $\alpha'$ 、 $\alpha''$ -トリピリジン0.5 g (2.1 mmol)と塩化クロム(III) THF錯体1.0 g (2.7 mmol)、塩化メチレン30 mlをアルゴン雰囲気下、室温で3時間攪拌し、析出した結晶をろ過し、式〔3〕の化合物である $\alpha$ 、 $\alpha'$ 、 $\alpha''$ -トリピリジクロム(III)クロリド0.68 gを得た(収率83%)。そのFDマスマスペクトル分析の結果を以下に示す。

FD-MS 390 (M<sup>+</sup>)

【0022】参考例2 式〔4〕の化合物の合成

攪拌および還流装置を備えた200 mlの容器に窒素雰

雰囲気下、ピリジン-2, 6-カルボキシアルデヒド3.0g (22.2mmol)、アニリン5.0g (53.4mmol)、メタノール100mlを入れ、50℃で8時間撹拌を行った。放冷した後、生じた結晶をろ過し、2, 6-ビス(2-フェニル-2-アザエテニル)ピリジン3.1gを得た(収率49%)。その<sup>1</sup>HNMRの結果を以下に示す。

<sup>1</sup>HNMR (CDCl<sub>3</sub>, δ, ppm)

7.20-7.60 (m, 10H)

8.01 (d, 1H, 9.0Hz)

8.32 (d, 2H, 9.0Hz)

8.76 (s, 2H)

【0023】得られた2, 6-ビス(2-フェニル-2-アザエテニル)ピリジン0.6g (2.1mmol)と塩化クロム(III) THF錯体1.0g (2.7mmol)、塩化メチレン30mlをアルゴン雰囲気下、室温で3時間撹拌し、析出した結晶をろ過し、式〔4〕の化合物である2, 6-ビス(2-フェニル-2-アザエテニル)ピリジクロム(III)クロリド0.85gを得た(収率72%)。そのFDマスペクトルの分析の結果を以下に示す。

FD-MS 442 (M<sup>+</sup>)

【0024】参考例3 式〔5〕の化合物の合成

ビス〔3-(2-ピリジルエチルイミノ)-2-ブタノンオキシム〕440mg (2.1mmol)とジクロロメタン20mlをアルゴン雰囲気下に撹拌し、三塩化クロムTHF錯体800mg (2.1mmol)ジクロロメタン溶液10mlを滴下した。室温で3時間撹拌した後、析出した結晶をろ過し、乾燥させ、式〔5〕の化合\*

表 1

\*物であるビス〔3-(2-ピリジルエチルイミノ)-2-ブタノンオキシム〕クロム(III)クロリドの緑色結晶530mgを得た(収率69%)。

【0025】実施例1

加熱乾燥した50ccのオートクレーブを加熱状態で組立てた後、真空窒素置換した。このオートクレーブに窒素雰囲気下、参考例1で得た式〔3〕の化合物(0.50mmol)、トリエチルアルミニウム(5.0mmol)およびトルエン10mlを加え、エチレンの全圧が30Kg/cm<sup>2</sup>になるまでエチレンを導入し、温度を130℃に維持した。1時間後、オートクレーブ中にエタノールを加え反応を停止した。オートクレーブの圧力を解除して脱ガスを行い、ガス分析をガスクロマトグラフィーにより行った。反応液中の生成物の分析もガスクロマトグラフィーにより行った。本実施例においてオートクレーブの内壁面を観察した結果、副生ポリマーの付着は認められなかった。ガスクロマトグラフィーによるα-オレフィン多量体の組成分析の結果を表1に示した。

【0026】実施例2~3、比較例1

実施例1において表1に示すように、触媒の種類を変えた以外は、実施例1と同様に反応操作を行った。ガスクロマトグラフィーによるα-オレフィン多量体の組成分析の結果を表1に示した。実施例2~3においてオートクレーブの内壁面を観察した結果、副生ポリマーの付着は認められなかった。比較例1の場合には、副生ポリマー付着が認められた。

【0027】

【表1】

	触 媒	選択率 (%)		触媒活性* (ターンオーバー)
		ヘキセン	その他	
実施例1	式〔3〕	77	23	11
実施例2	式〔4〕	59	41	128
実施例3	式〔5〕	42	58	6
比較例1	CrCl <sub>3</sub>	9	91	330

\*オリゴマー生成量より、エチレン基準で算出

【0028】

【発明の効果】本発明によれば、特定の触媒を用いることにより、特定のα-オレフィン多量体を選択的に効率よく製造することができ、特にα-オレフィンとしてエ※

※チレンを用いる場合、線状低密度ポリエチレン(LLDPE)のコモノマーとして有用な1-ヘキセンを選択的に効率よく製造することができる。

## 【手続補正書】

【提出日】平成8年9月12日

## 【手続補正1】

【補正対象書類名】明細書

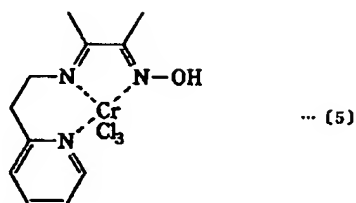
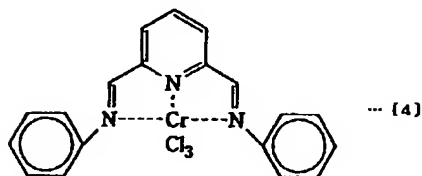
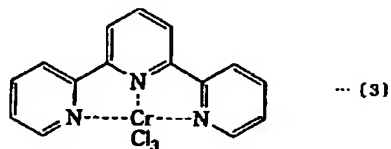
【補正対象項目名】請求項2

【補正方法】変更

【補正内容】

【請求項2】 遷移金属化合物が式〔3〕～〔5〕で示される化合物から選ばれるものである請求項1記載の方法。

【化3】



## 【手続補正2】

【補正対象書類名】明細書

【補正対象項目名】0006

【補正方法】変更

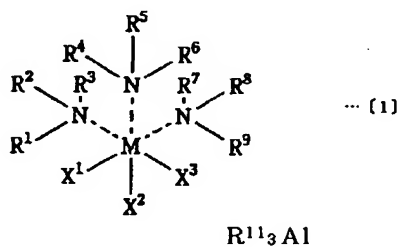
【補正内容】

【0006】

【課題を解決するための手段】本発明は次の $\alpha$ -オレフィン多量体の製造方法である。

(1) 一般式〔1〕で示される遷移金属化合物と、一般式〔2〕で示されるアルミニウム化合物との存在下に、 $\alpha$ -オレフィンを反応させる工程を含む $\alpha$ -オレフィン多量体の製造方法。

【化5】



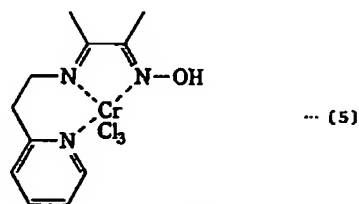
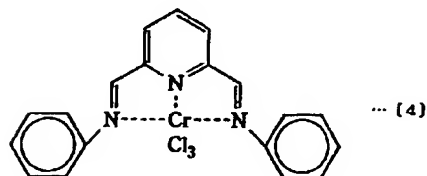
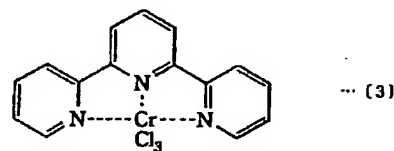
〔式中、Mは遷移金属であり、 $R^1 \sim R^9$ はそれぞれ水素原子、水酸基、直鎖または分岐状のアルキル基、アルケニル基もしくはアリール基であって、同一でも異なってもよく、置換基を有していてもよく、相互に結合して環または架橋を形成していてもよく、また2個が合体してアルキリデン基、アルケニリデン基もしくはアリーリデン基を形成していてもよく、 $X^1 \sim X^3$ は水素原子、ハロゲン原子、直鎖または分岐状のアルキル基であって同一でも異なってもよく、置換基を有していてもよい。〕

【化6】  $R^{11}_m Al(OR^{12})_n X_p H_q$  ...〔2〕

〔式中、 $R^{11}$ 、 $R^{12}$ はそれぞれ炭素数1～15の炭化水素基であり、同一でも異なってもよく、Xはハロゲン原子を表す。 $m$ は $0 < m \leq 3$ 、 $n$ は $0 \leq n < 3$ 、 $p$ は $0 \leq p < 3$ 、 $q$ は $0 \leq q < 3$ のそれぞれの数であり、 $m + n + p + q = 3$ である。〕

(2) 遷移金属化合物が式〔3〕～〔5〕で示される化合物から選ばれるものである上記(1)記載の方法。

【化7】



(3) アルミニウム化合物が一般式〔6〕～〔9〕から選ばれるものである上記(1)または(2)記載の方法。

【化8】

...〔6〕

$$R^{11} \cdot AlX_{3-m} \quad (mは1.5 \leq m < 3) \quad \dots [7]$$

$$R^{11} \cdot Al(OR^{12})_{3-m} \quad (mは0 < m < 3) \quad \dots [8]$$

$$R^{11} \cdot AlH_{3-m} \quad (mは0 < m < 3) \quad \dots [9]$$

〔式中、 $R^{11}$ 、 $R^{12}$ はそれぞれ炭素数1～15の炭化水素基であり、同一でも異なってもよく、Xはハロゲンを表す。〕

【手続補正3】

【補正対象書類名】明細書

【補正対象項目名】0013

【補正方法】変更

【補正内容】

【0013】このような一般式〔1〕で示される遷移金属化合物の好ましい例として、前記式〔3〕～〔5〕のものがあげられる。式〔3〕の化合物は $\alpha$ 、 $\alpha'$ 、 $\alpha''$ -トリピリジンクロム(III)クロリドであり、 $\alpha$ 、 $\alpha'$ 、 $\alpha''$ -トリピリジンと塩化クロム(III)THF(テトラヒドロフラン)錯体とを反応させて製造することができる。式〔4〕の化合物は2,6-ビス(2-フェニル-2-アザエチル)ピリジンクロム(III)クロリドであり、2,6-ビス(2-フェニル-2-アザエチル)ピリジンと塩化クロム(III)THF錯体とを反応させて製造することができる。式〔5〕の化合物は〔3-(2-ピリジリエチルイミノ)-2-ブタノンオキシム〕クロム(III)クロリドであり、〔3-(2-ピリジリエチルイミノ)-2-ブタノンオキシム〕と三塩化クロムTHF錯体とを反応させて製造することができる。

【手続補正4】

【補正対象書類名】明細書

【補正対象項目名】0015

【補正方法】変更

【補正内容】

【0015】このような一般式〔2〕のアルミニウム化合物の好ましい化合物として、前記一般式〔6〕～〔9〕の化合物があげられる。一般式〔6〕～〔9〕において $R^{11}$ 、 $R^{12}$ としては炭素数1～15、好ましくは1～8のアルキル基、アルケニル基またはアリール基が

好ましい。一般式〔8〕、〔9〕において、 $m$ は $0 < m < 3$ 、好ましくは $1.5 \leq m < 3$ である。

【手続補正5】

【補正対象書類名】明細書

【補正対象項目名】0018

【補正方法】変更

【補正内容】

【0018】溶媒としてはペンタン、ヘキサン、シクロヘキサン、メチルシクロヘキサン、ヘプタン、オクタン、デカリン等の直鎖状または脂環式の飽和炭化水素、ベンゼン、トルエン、エチルベンゼン、キシレン、メシチレン、テトラリン等の芳香族炭化水素、ジクロロメタン、クロロホルム、四塩化炭素、ジクロロエタン等の鎖状塩素化炭化水素、クロロベンゼン、ジクロロベンゼン等の塩素化芳香族炭化水素などが使用される。これらは単独であるいは混合溶媒として使用することができる。特にベンゼン、トルエン、エチルベンゼン、キシレン、メシチレン、テトラリン等の芳香族炭化水素が高い触媒活性が得られるため好適である。

【手続補正6】

【補正対象書類名】明細書

【補正対象項目名】0024

【補正方法】変更

【補正内容】

【0024】参考例3 式〔5〕の化合物の合成  
〔3-(2-ピリジリエチルイミノ)-2-ブタノンオキシム〕440mg(2.1mmol)とジクロロメタン20mlをアルゴン雰囲気下に攪拌し、三塩化クロムTHF錯体800mg(2.1mmol)ジクロロメタン溶液10mlを滴下した。室温で3時間攪拌した後、析出した結晶をろ過し、乾燥させ、式〔5〕の化合物である〔3-(2-ピリジリエチルイミノ)-2-ブタノンオキシム〕クロム(III)クロリドの緑色結晶530mgを得た(収率69%)。